

Cathodically pretreated poly(1-aminoanthraquinone)-modified electrode for determination of ascorbic acid, dopamine, and uric acid

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Abstract This paper describes a rapid and reliable method for dopamine (DA), ascorbic acid (AA), and uric acid (UA) determination in human urine using a cathodically pretreated poly(1-aminoanthraquinone) (PAAQ)-modified electrode. By applying a simple cathodic pretreatment to the PAAQ electrode well-defined voltammetric peaks for AA, DA, and UA were obtained. The pretreated PAAQ showed good selectivity, sensitivity, and repeatability for measuring AA, DA, and UA with detection limits of 2.50×10^{-5} , 3.05×10^{-6} , and 1.15×10^{-5} M, respectively. The practical applicability of the modified electrode is illustrated by selective measurements of AA and UA in human urine without any preliminary treatment. Recovery values between 94.8 and 102 % for AA and between 77.8 and 100 % for UA were obtained with a relative standard deviation of 2.74 and 2.98 %, respectively.

Keywords Dopamine · Ascorbic acid · Uric acid · Cathodic pretreatment · Conducting polymer · Poly(1-aminoanthraquinone)

1 Introduction

The electrochemical determination of dopamine (DA) in biological fluids at bare electrodes is hampered by undesirable interference from ascorbic acid (AA) and uric acid (UA) [1, 2]. The development of a simple and fast electroanalytical method to determine DA, AA, and UA in

biological samples with good selectivity and sensitivity is still a significant challenge. To overcome this shortcoming, different materials, including particles and nanoparticles of metal and metal oxides [3, 4], carbon compounds such as graphene and carbon nanotubes [5–7], metal complexes, and organic compounds [8, 9], have been used to construct new electrochemical sensors. In this context, significant advantages have been achieved using conducting polymers (CPs) to develop electrochemical sensors for measuring organic and inorganic compounds. CPs can be easily prepared as film electrodeposited over different substrates with good homogeneity, chemical stability, and adherence, with the possibility of incorporating different materials to form composites. Electrodes modified with CPs have been applied in the determination of catecholamines in different samples such as pharmaceutical formulations and biological fluids [10–14]. However, in most cases it is necessary to incorporate one of the materials aforementioned into the polymer to form a composite [9, 15–21] or overoxidize the polymer [9, 22–25] to achieve electrocatalytic response for DA detection. Recently, we demonstrated the influence of cathodic pretreatment of the aromatic-amine derivate conducting the polymers poly(1-aminoanthracene) (PAA) [12] and poly(1,5-diaminonaphthalene) (PDAN) [26] for detecting DA and norepinephrine, respectively. In those studies, PAA presented a reversible response for DA only after cathodic pretreatment. Meanwhile PDAN could display an electrochemical response for NE without pretreatment, but the voltammetric response was improved when cathodic pretreatment was applied. In both cases, the pretreated electrodes showed no interference from AA in the electroanalytical responses for the catecholamines. These very interesting electrochemical behaviors might have been due to the chemical and conformational changes of the polymer, which led to modifications in their properties such

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as the kinetics of charge transfer, rate coefficients, and activation energies [27–31].

In this work, we developed a conducting film of poly(1-aminoanthraquinone) (PAAQ) on a platinum electrode and evaluated the influence of cathodic pretreatment on the electrocatalytic response for DA, AA, and UA detection. We demonstrated that cathodically pretreated PAAQ offered an effective oxidation peak separation of DA, UA, and AA. Furthermore, this method was used to measure UA and AA in human urine samples.

2 Experimental

2.1 Apparatus

All voltammetric experiments were performed using a potentiostat Autolab model PGSTAT-128N (Netherlands). A conventional three-electrode electrochemical system was used for all electrochemical experiments, which consisted of a Pt disk electrode with a geometric area of 0.031 cm^2 used as the working electrode, a platinum plate as the counter electrode, and Ag/AgCl (3.0 M KCl) as the reference electrode. An Ag wire quasi-reference electrode was used for producing the PAAQ in non-aqueous solution. Water used in the experiments was purified by the Millipore model Milli-Q system (USA).

2.2 Reagents

AA, DA, UA, LiClO_4 , and 1-aminoanthraquinone (1-AAQ) were purchased from Sigma-Aldrich (USA) and used as received. The stock solutions of DA (0.010 M) and AA (0.010 M) were prepared daily by dissolving DA hydrochloride and AA in water. UA solution (0.010 M) was prepared by previous dissolution of the solid in 0.1 M NaOH solution and diluted with water to the desired concentration. Prior to the electrochemical measurements, the solutions were deaerated by purging with nitrogen gas.

2.3 Preparation of PAAQ-modified electrode

Before each experiment, the Pt electrode was polished with 1.0 and $0.3\text{ }\mu\text{m}$ sized alumina powder in a water surry using a polishing cloth, washed with water, and sonicated in distilled water for about 10 min. After that, the polished electrode was placed in 0.5 M H_2SO_4 solution and cycled in the potential range of -0.2 to $+1.2\text{ V}$ at a scan rate of 0.05 V s^{-1} until the characteristic profile of Pt was obtained, then washed with water and dried under nitrogen flow. The electrode was subsequently placed in a solution containing 0.1 M LiClO_4 and 0.010 M 1-AAQ monomer in acetonitrile, before this a cyclic voltammetry was applied

in the range of -0.1 to $+1.3\text{ V}$ at a scan rate of 0.1 V s^{-1} . After polymerization, the PAAQ electrode was rinsed with acetonitrile and then water.

2.4 Procedure for DA, AA, and UA measurements

Effects of the influence of film synthesis, differential pulse voltammetry (DPV) and square wave voltammetry (SWV) parameters, cathodic pretreatment, pH, and electrolyte solutions on the electrochemical response of DA were studied. After attaining the background voltammogram, aliquots of the sample solution containing AA, DA, and UA were introduced into the cell containing supporting electrolyte. All data were obtained at room temperature. Analytical curves were prepared by plotting the net peak currents as function of AA, DA, and/or UA concentrations. Before each voltammetric measurement, a cathodic pretreatment was performed on PAAQ electrode, which consisted of applying a constant potential for a certain period of time. The cathodically pretreated electrode was then denoted as p-PAAQ.

2.5 Real sample analysis

Urine samples were collected from healthy volunteers and used immediately after collection without further preparations. The standard addition method was used for analyzing the urine samples in which a certain amount of sample was added to the electrochemical cell containing phosphate buffered solution (PBS), pH 7.0, with three successive additions of AA or UA standard solution and SWV to perform the measurements.

3 Results and discussion

3.1 Synthesis of the PAAQ

Figure 1 displays the cyclic voltammograms of PAAQ electropolymerization in the range -0.1 to $+1.3\text{ V}$ at 0.1 V s^{-1} over 10 cycles in a solution of $10 \times 10^{-3}\text{ M}$ 1-AAQ and 0.1 M LiClO_4 in acetonitrile. During the polymerization process, an irreversible anodic current started near $+1.15\text{ V}$ in the first cycle was observed and corresponded to monomer oxidation. According to the literature [32], this peak could be attributed to the oxidation of the amino group, which forms a radical cation and subsequently the polymeric chain. A small peak was observed during the reverse scan, at a potential of approximately $+0.80\text{ V}$, which increased during continuous cycling. Finally, two pairs of cathodic and anodic peaks were observed near $+0.65$ and $+1.00\text{ V}$, respectively, after continuous cycling, and were related to the

growth of the polymer film on electrode surface. Therefore, after 10 cycles, a uniform and adherent dark gray film was formed on the platinum electrode surface.

3.2 DA electrocatalytic responses at the PAAQ-modified electrode

The influence of cathodic pretreatment of the PAAQ electrode on DA electrochemical response was evaluated. Figure 2 shows the electrochemical response of 56.0×10^{-6} M DA in 0.1 M PBS pH 7.0 at the PAAQ electrode obtained by DPV, with (solid line) and without (dotted line) cathodic pretreatment, which consisted of applying a potential of -0.7 V for 3 s before each measurement. The PAAQ and pretreated PAAQ electrodes (p-PAAQ) presented a response for DA with peak potentials at 0.17 and 0.15 V (vs. Ag/AgCl), respectively. It should be noted that p-PAAQ displayed a DA peak current three times higher than PAAQ that was not pretreated. A similar behavior has already been observed previously for PAA [12] and PDAN [26] demonstrating that the cathodic pretreatment changed the electrocatalytic property of the polymeric film. This might be related to chemical and conformational changes in the polymer films [29, 30, 33] leading to the modifications in their electrocatalytic properties.

3.3 Parameters of PAAQ synthesis and DA determination

The PAAQ synthesis conditions were optimized and taken into account the best analytical performance for DA determination. The study parameters were monomer concentration (1 to 50×10^{-3} M), type (LiClO_4 and TBAP) and concentration of the supporting electrolyte (0.01 – 0.5 M) and the number of polymerization cycles (5 – 50 cycles). The best conditions were defined as the parameters that

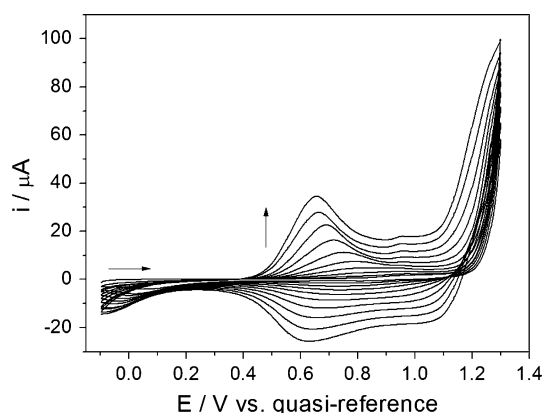


Fig. 1 Cyclic voltammograms of PAAQ film formation obtained in solution of 10×10^{-3} M 1-AAQ and 0.1 M LiClO_4 in acetonitrile at a scan rate 0.1 V s^{-1} and for 10 cycles

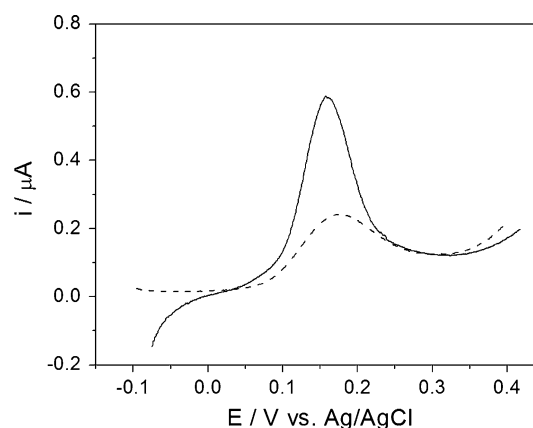


Fig. 2 Differential pulse voltammograms of the PAAQ electrode obtained in 56.0×10^{-6} M DA in PBS, pH 7.0, solution, with (solid line) and without (dashed lines) cathodic pretreatment of the electrode

presented maximum peak current and good peak profile obtained in a solution of 5.0×10^{-5} M DA in PBS pH 7.0. For this purpose a series of SWV experiments were carried out and the results were obtained with a monomer concentration of 10.0×10^{-3} M, 0.1 M of LiClO_4 , at 10 cycles and with a scan rate of 0.1 V s^{-1} .

The pH of the solution significantly affected DA oxidation at the modified electrode, affecting both peak current and peak potential, as can be observed in Fig. 3A. For the voltammograms obtained with 5.0×10^{-5} M DA in the pH range of 5.81–8.02, the peak potential showed a linear variation toward a more negative potential when the pH increased. The linear relationship between peak potential and pH, exhibiting a linear regression equation of $E_p \text{ (V vs. Ag/AgCl)} = 0.51 - 0.049 \text{ pH}$ and $r = 0.992$ (Fig. 3B), indicated a correlation between protons and electrons of one as expected for the oxidation of DA. The maximum current was obtained in PBS at pH 7.0 and as a result, this solution was chosen for subsequent experiments. The electrochemical response of DA was also studied in Britton–Robinson buffer solution (B–R); however, the peak current obtained in PBS was about two times higher than that in B–R (data not shown).

The application of pretreatment on the conducting polymer electrodes was of great importance in the electrocatalytic response and consequently, in the determination of the analytes. In this way, the influence of the different pretreatment conditions on DA measurement was evaluated by SWV and the results are presented in Fig. 4A. As can be seen from Fig. 4B, the anodic peak current increased when a more negative potential was applied during PAAQ pretreatment. In this case each potential was applied for 3 s starting at -0.1 V until -1.2 V. Pretreatment with the potential of -0.9 V generated the highest current response for DA. Figure 4C shows the variation of the peak current for DA oxidation as a function of the

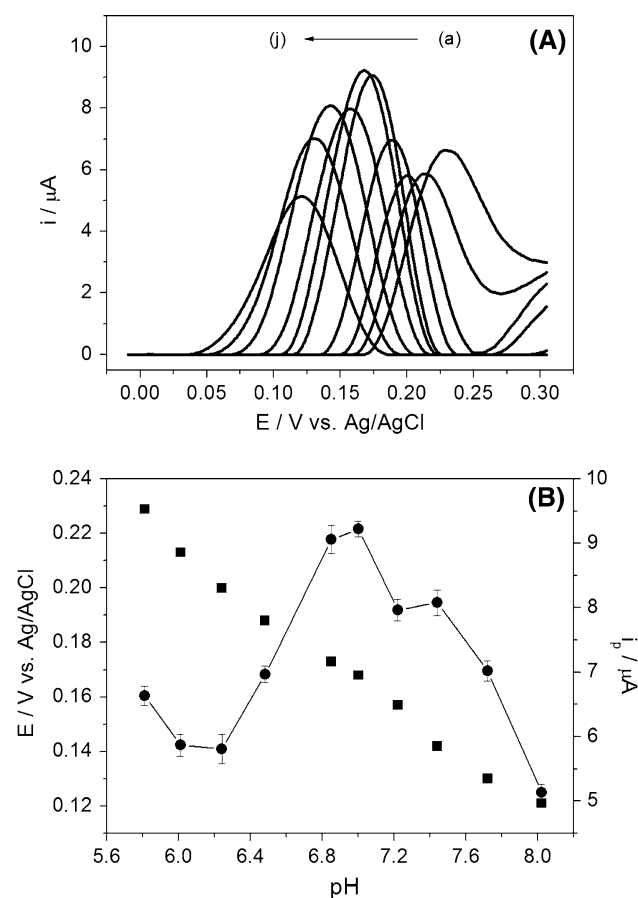


Fig. 3 **A** SWVs obtained using p-PAAQ electrode in 5.0×10^{-5} M DA solutions with different pH values of (a) 5.81, (b) 6.00, (c) 6.24, (d) 6.48, (e) 6.85, (f) 7.00, (g) 7.22, (h) 7.40, (i) 7.72, and (j) 8.02. **B** Dependence of the peak potential (filled square) and peak current (filled circle) on pH

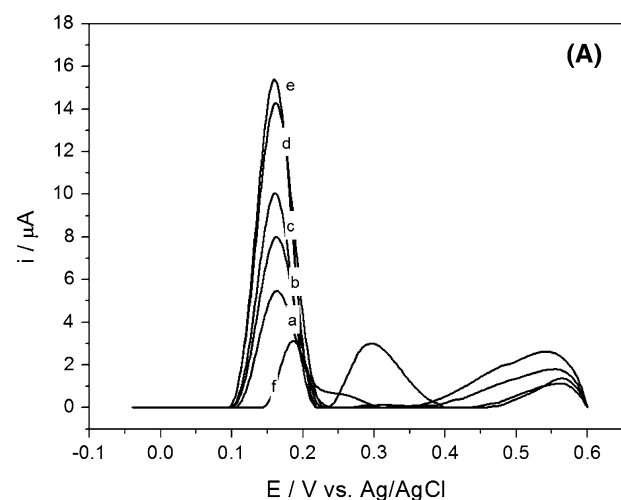


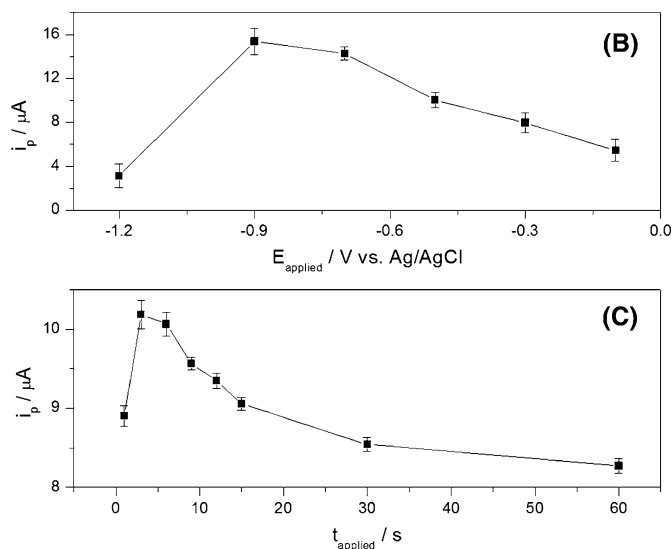
Fig. 4 **A** Influence of PAAQ pretreatment on the peak current obtained for DA by SWV. Applied potentials (V) for 3 s: (a) -0.1, (b) -0.3, (c) -0.5, (d) -0.7, (e) -0.9, and (f) -1.2. Dependence of

polarization time for a potential of -0.9 V. Pretreatment with a polarization time of 3 s gave the highest peak current. Therefore, the potential of -0.9 V for 3 s was selected for subsequent experiments.

From Fig. 4C, it is possible to infer that cathodic pretreatment for longer than 3 s did not elicit a preconcentration of DA at the electrode surface once the peak currents decreased. This indicated that cathodic pretreatment changed the electrocatalytic properties of the PAAQ for DA oxidation.

To establish the optimum conditions for measuring DA, the influence of SWV parameters was evaluated in 5.0×10^{-5} M DA solution. The square wave frequency (f), pulse amplitude (a), and scan increment (ΔE_s) were investigated and the obtained optimum values for the determination of DA were 10 s^{-1} , 0.06 and 0.001 V, respectively.

The analytical curve for DA in PBS pH 7.0 was constructed measuring the peak current obtained at different concentrations of DA with the p-PAAQ electrode by SWV (data not shown). The anodic peak currents exhibited a good linear relationship with DA in the concentration range of $3.07\text{--}1.04 \times 10^{-5}$ M. The linear regression equation obtained was $\Delta i_p (\mu\text{A cm}^{-2}) = -1.63 + 0.047 [\text{DA}] (\text{M})$, with a correlation coefficient of 0.9977. The detection limit was calculated using the equation $3s_b/m$, where s_b is the standard deviation of the blank response and m the slope of the analytical curve. The detection limit for DA was estimated to be 1.25×10^{-6} M. The repeatability of the p-PAAQ electrode measurements was evaluated and taken into account the peak current responses for ten successive DA measurements in a solution of 3.4×10^{-5} M DA. The



the anodic peak current as function on **B** the potential applied for 3 s and **C** the potential of -0.9 V applied for different times. The solution used was of 5.4×10^{-5} M DA in 0.1 M PBS, pH 7.0

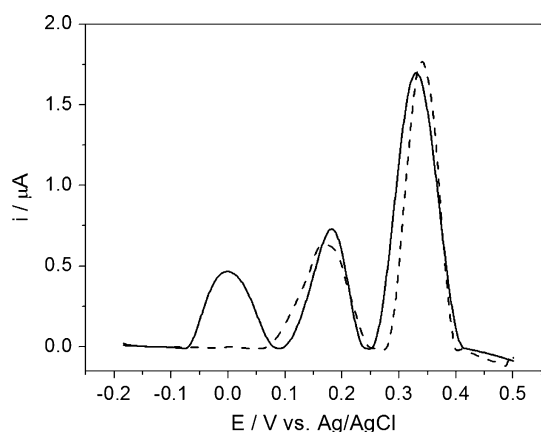


Fig. 5 SWVs at the PAAQ (dash line) and p-PAAQ (solid line) electrode in 0.1 M PBS (pH 7.0) containing 5.3×10^{-4} M AA, 3.4×10^{-5} M DA, and 5.4×10^{-4} M UA

p-PAAQ electrode exhibited good repeatability with a relative standard deviation of 4.42 %.

3.4 Simultaneous measurement of AA, DA, and UA at the p-PAAQ electrode

To find a selective and sensitive method using the modified p-PAAQ electrode to simultaneously detect DA, AA, and UA, the application of cathodic pretreatment was investigated. As shown in Fig. 5, the SWV obtained in a mixture of DA, AA, and UA solution presented two peaks at about 0.17 and 0.34 V at the PAAQ electrode (dash line) corresponding to the overlapping AA and DA, and UA, respectively. In this case, the broad and overlapping voltammetric peaks did not allow us to obtain analytical information about DA and AA using the non-pretreated PAAQ. On the other hand, at the p-PAAQ electrode, the overlapping voltammetric peaks were resolved and three well-defined peaks (solid line) at about 0.00, 0.18, and 0.32 V were obtained, corresponding to the oxidation of AA, DA, and AU, respectively. The cathodic pretreatment of PAAQ led to good peaks separation allowing the determination of AA, DA, and UA individually.

The influence of concentration of the different analytes on the electrochemical responses at the p-PAAQ electrode was studied. The oxidation processes of DA, AA, and UA were investigated by SWV and varying the concentration of each analyte while maintaining the concentrations of the other two species constant. The results are shown in Fig. 6. The peak currents for each analyte increased linearly with their concentration, when the concentrations of the two other species were kept constant. The analytical parameters for measuring AA, DA, and UA are listed in Table 1. The results obtained are comparable with the values obtained by other analytical methods (Table 2). The results obtained with the cathodically pretreated PAAQ suggest that AA,

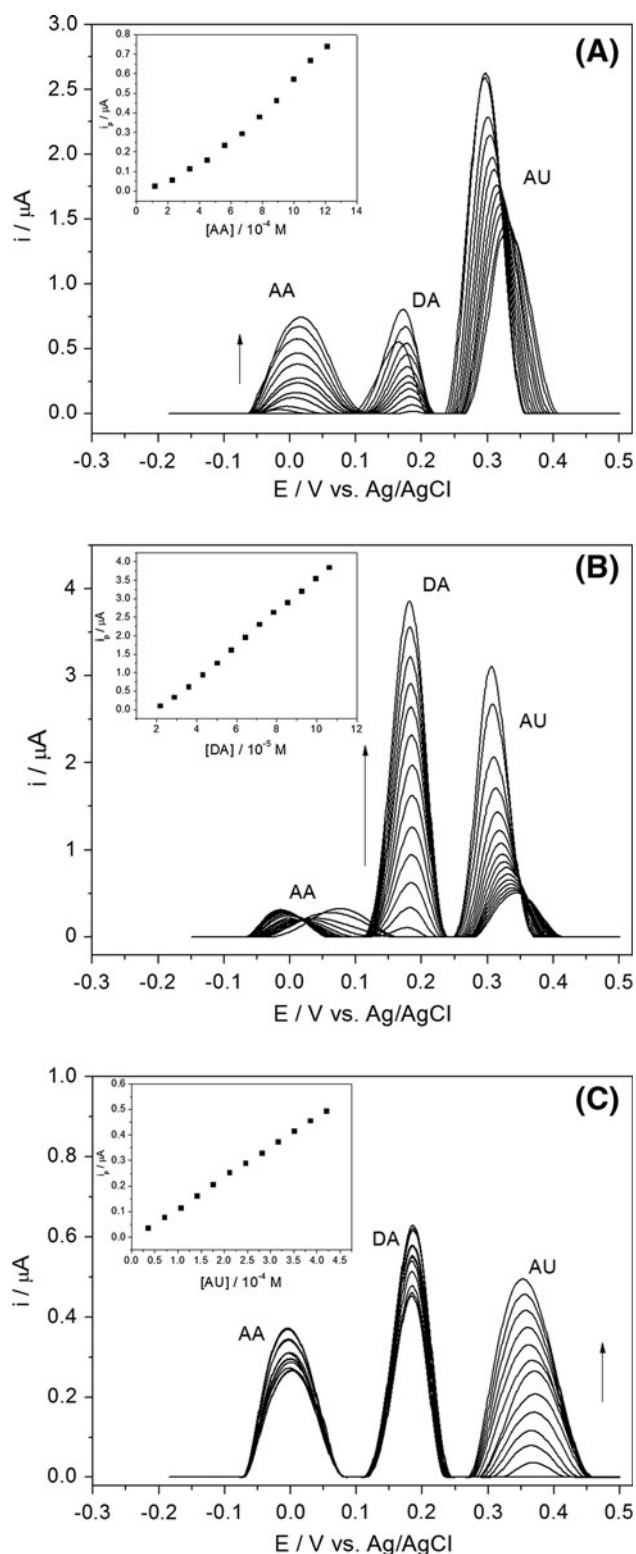


Fig. 6 SWVs at the p-PAAQ electrode in 0.1 M PBS (pH 7.0) containing **A** 3.23×10^{-5} M DA, 6.5×10^{-4} M AU and different concentrations of AA ranging from 1.12 to 12.1×10^{-4} M; **B** 5.6×10^{-4} M AA, 5.4×10^{-4} M AU and different concentrations of DA from 7.20 to 106×10^{-6} M; **C** 5.6×10^{-4} M AA, 2.8×10^{-5} M DA and different concentrations of UA ranging from 3.52 to 41.9×10^{-4} M. Inset analytical curves

Table 1 Analytical parameters for measuring DA, AA, and UA

Analyte	Linear range ($\times 10^{-5}$ M)	Linear regression equation (Δi_p : μ A; C : mM)	Correlation coefficient (r)	Detection limit ($\times 10^{-5}$ M)
AA	11.2–121	$\Delta i_p = -0.11 + 0.67C$	0.9778	2.50
DA	2.15–10.6	$\Delta i_p = -0.005 + 0.12C$	0.9989	0.305
UA	3.50–42.0	$\Delta i_p = -0.95 + 45C$	0.9996	1.15

Table 2 Comparison of different-modified electrodes for the detection of AA, DA, and UA

Modified electrodes	pH	Linear range (μ M)			Detection limit (μ M)			Sample	References
		AA	DA	UA	AA	DA	UA		
GCE/polybromothymol blue	5.0	1.0–800	8.0–150	0.1–50	1.0	0.01	1.0	Injection solutions	[34]
GCE/ <i>p</i> -phenylenediamine	5.0	2.0–2000	10.0–1,250	50.0–1,600	0.4	1.0	2.5	Human serum	[35]
GCE/graphene nanofibers/ionic liquid/chitosan	6.0	30–350	0.05–240	0.12–260	14.8	0.05	0.10	Human urine	[36]
GCE/single-walled carbon nanohorn	7.0	30–400	0.2–3.8	0.06–10	5.0	0.06	0.02	Human urine	[37]
GCE/poly(2-amino-1,3,4-thiadiazole)	5.0	30–300	5–500	10–100	2.01	0.33	0.19	Human urine	[14]
GCE/chitosan–graphene	7.0	50–1,500	1.0–24	2.0–45	50	1.0	2.0	Not reported	[38]
GCE/Au and Pt nanoparticles	4.0	24–384	103–165	21–336	103	24	21	Injection solutions	[39]
Ni/silicon microchannel/PEDOT	7.4	20–1,400	12–48	36–216	10	1.5	2.7	Human urine	[40]
Pt/PAAQ	7.0	112–1,210	21.5–106	35–420	25	3.05	11.5	Human urine	This work

Table 3 Recovery studies of AA and UA in human urine samples using p-PAAQ

Analyte	Spiked (10^{-4} M)	Found ^a (10^{-4} M)	Recovery (%)
AA	2.80	2.66 ± 0.01	94.8
	4.19	4.28 ± 0.03	102
	6.95	6.75 ± 0.01	97.1
UA	1.17	0.91 ± 0.01	77.8
	1.75	1.43 ± 0.01	81.4
	2.33	2.33 ± 0.01	100

^a Results are expressed as average \pm SD based on three replicates

DA, and UA can be selectively determined in complex samples.

The p-PAAQ electrode was used for recovery studies in real samples of human urine. Once the basal level of DA in healthy urine samples was above the limit of detection for p-PAAQ, recovery studies were performed with AA and UA. These tests were carried out by adding a known amount of AA or UA to the urine samples followed by detecting the analytes using the standard addition method. All measurements were performed in triplicate. Recovery values of between 94.8 and 102 % for AA and 77.8–100 % for UA were obtained (Table 3). For the lowest concentration of UA the recovery showed low values, probably due to the low oxidation current obtained for UA. The p-PAAQ electrode exhibited good repeatability with a relative standard deviation of 2.74 and 2.98 % for 5.3×10^{-4} M AA and UA, respectively.

4 Conclusions

In this paper, we describe a novel method for AA, DA, and UA detection based on a use of cathodically pretreated poly(1-aminoanthraquinone)-modified electrode. A simple cathodically pretreatment, that consisting of applying a potential of -0.9 V (vs. Ag/AgCl) for 3 s before each measurement, yielded good peak separation for AA, DA, and UA. The cathodically pretreated PAAQ presented good selectivity, sensitivity, and repeatability, with good detection limits for AA, DA, and UA, giving values of 2.50×10^{-5} , 3.05×10^{-6} , and 1.15×10^{-5} M, respectively. Therefore, cathodically pretreated PAAQ electrodes can be used for determining DA, AA, and UA with good sensitivity and selectivity.

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